

Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

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University of Texas at Austin

Submitted by:

Dr. David Allen
(allen@che.utexas.edu)
512-471-0049

Center for Energy and Environmental Resources
The University of Texas at Austin
10100 Burnet Road, Bldg. 133
MS R7100
Austin, Texas 78758

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Title: Gulf Coast Aerosol Research and Characterization Study

Investigators: Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)

Institutions: University of Texas and Rice University

Research Category: Air Quality/Fine Particulate Matter

Project Period: 01/15/00-11/30/03

Objective of Research: Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas

Progress Summary/Accomplishments:

Analysis of data collected during the Houston Supersite field program is transitioning from descriptive analysis of the data to source resolution. This quarterly report describes some of the work done to date on anthropogenic sources of secondary organic aerosol.

Overview

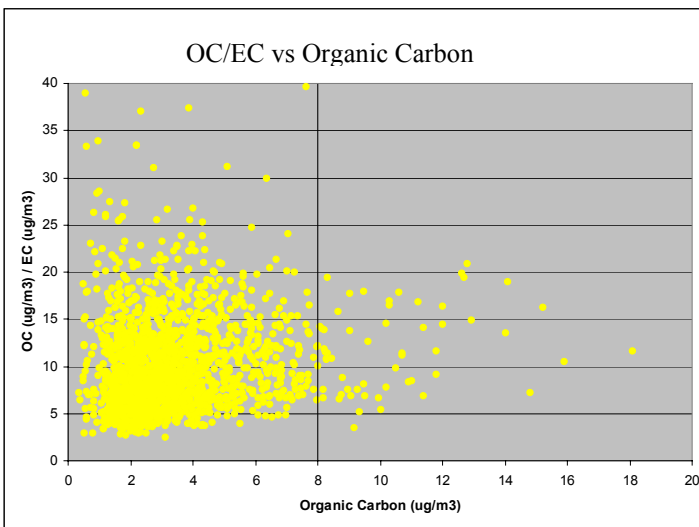
Secondary Organic Aerosol (SOA) formation due to precursor emissions from anthropogenic sources in the Houston/Galveston (HG) area was estimated by multiplying the anthropogenic emissions of SOA precursors by fractional aerosol coefficients (FAC). The analysis indicated that emissions of terpenes from pulp and paper processing and emissions of aromatics, especially toluene, xylenes and trimethylbenzenes are significant SOA precursors in the Houston-Galveston (HG) area. Estimated SOA formation rates were consistent with average concentrations of particle phase organic carbon in the Houston-Galveston area. The yield of SOA from aromatic precursors was examined further using box model simulations, including SOA formation mechanisms and gas/particle partitioning. These calculations suggest that SOA formation rates are sensitive to both aromatic precursor emissions and NO_x emissions, and the pattern of the sensitivity is similar to the pattern of ozone sensitivity to hydrocarbon and NO_x emissions for the Houston area.

Background

Annual average fine particulate matter concentrations over much of the Houston-Galveston area in Texas approach the National Ambient Air Quality Standard of $15 \mu\text{g}/\text{m}^3$. On average, approximately 25% of the mass is carbonaceous (Tropp, et al, 1998), and most of the carbonaceous material is characterized as organic carbon (OC), where OC is defined as carbon containing materials that volatilize below approximately 850°C in a thermogravimetric analysis. Only a small fraction of the carbon is in light-absorbing, soot-like structures, commonly referred to as elemental carbon, or EC. The sources of OC in fine particulate matter can be either direct emissions to the atmosphere (primary organics), or secondary organic aerosol (SOA) formation. SOA is formed in the atmosphere through the reactions of gas phase organics, which produce low volatility reaction products.

The ratio of OC to EC is often used to distinguish the relative importance of primary and secondary organics. It is generally assumed that soot-like EC is only emitted by primary (combustion) sources, and that these primary emissions have some characteristic ratio of OC to EC. A ratio between 2 and 5 is generally assumed for OC/EC in primary emissions (Strader, et al., 1999). If observed ratios of OC/EC are higher than those assumed to occur in primary emissions then the excess OC is assumed to be due to secondary organic aerosol formation. Figure 1 shows that OC to EC ratios in southeast Texas are generally well above the value assumed for primary emissions, suggesting that much of the OC may be due to secondary organic aerosol formation.

Figure 1. Daily average OC to EC ratios in fine particulate matter (PM_{2.5}) in southeast Texas; measurements are at multiple sites for the period 1999-2001 (Russell, et al., 2002)



Estimates of SOA formation can also be based on emission rates of SOA precursors and predicted yields of SOA from those precursors. In the models most commonly used to estimate SOA formation, the extent of hydrocarbon reaction and the selectivity of gas phase reactions to SOA is assumed to be constant. These overall yields of SOA are referred to as fractional aerosol coefficients (FACs), and FACs have been estimated for a large number of hydrocarbons (Grosjean and Seinfeld, 1989). The advantage of a FAC is that it allows SOA yield to be estimated directly from emission inventory data, however, assuming constant yields for the hydrocarbon reactions is a gross simplification. Recently, more sophisticated approaches have been developed that account for increases in SOA yield as the mass of the aerosol phase increases and models have been developed that couple SOA formation chemistry and phase partitioning into comprehensive gas phase mechanisms for hydrocarbon reactions. Currently, however, these more advanced SOA models are available for only a limited number of compounds.

In this work, the emission rates of SOA precursors from anthropogenic sources in the Houston/Galveston area will be estimated and SOA yields will be estimated using both FACs and more detailed mechanistic models. Data obtained during the Texas Air Quality Study (TexAQS) 2000 will be used to semi-quantitatively assess the accuracy of the predictions. Finally, the response of SOA formation to emission reduction strategies will be assessed using detailed mechanistic models.

Methods

Emission Inventories

To estimate rates of SOA formation, a speciated inventory of SOA precursors was assembled for point sources, area sources, non-road sources and on-road mobile sources for the domain shown in Figure 2. The methods and data sources used in creating the inventory are described below.

Point Sources

The Texas Commission on Environmental Quality (TCEQ, formerly the Texas Natural Resource Conservation Commission, TNRCC) has prepared a speciated volatile organic compound (VOC) point source inventory for the state of Texas for 2000 (TCEQ, 2002). Emissions are listed by stack, by VOC species (or mixture) in tons per day for a typical ozone season day. A total of 226 tons per day of VOC emissions were reported from the Houston/Galveston point source database including 12,536 individual points at 481 separate accounts (Neece, 2001). VOC emissions are assigned specific compositions using speciation profiles. In the HG area, there are 4,195 point source profiles (Neece, 2001). Speciation profiles contain the mass fractions of individual organic compounds (approximately 510 compounds) typically emitted from the point sources (Neece, 2001). A small fraction of the sources are not speciated and list emissions as ‘total reactive VOC’. These emissions (less than 1% of the mass reported) were not considered in the calculations reported here.

Of the more than 500 compounds/mixtures identified in the point source inventory, the 100 compounds emitted at the greatest rates accounted for 96% of the inventory (217 tons per day, see Table 1), so SOA yield calculations focused only on these compounds. Many of the top 100 compounds were of low molecular weight (less than 6 carbon atoms) and their SOA yields were assumed to be negligible. The remaining emissions were characterized as potential SOA precursors, and accounted for 44 tons per day of the total emissions. Of these SOA precursors, FAC data were available for precursors accounting for 43 tons per day of emissions; FACs for the remaining compounds (1 ton/day) were based on FACs of structurally similar compounds. A complete listing of all compounds, and the FAC values used in the SOA calculations is available from the authors.

Table 1: Point source inventory

	Tons/day	% of total
Total point source emissions in study area	226	100%
Sources designated as unspeciated	2.0	< 1%
Emissions of top 100 compounds/mixtures	217	96%
Emissions from SOA precursor compounds/mixtures	44	20%
Emissions from SOA precursors with FAC estimates	43	19%
Emissions from SOA precursors without FAC estimates	1	0.4%



Figure 2: Study Domain

Area and Nonroad Sources

Area source emissions in the study area were taken from a state-wide, county-level 1999 emission inventory (ENVIRON, 2002). This inventory was based largely on the National Emission Inventory (NEI) 1999 Version 1 for Criteria Pollutants, released by EPA 20 March 2001 (Jimenez, 2002). Area and nonroad emissions in this inventory are reported by county, by 12-digit SCC code (Source Classification Code) and as total reactive VOC. The SCC is a hierarchical representation of emission sources. For example, SCC 2270004041 represents “Mobile Sources/ Off-highway Vehicle Diesel/ Lawn and Garden Equipment/ Rear Engine Riding Mowers (Commercial)”. The first 2 digits “22” designate Mobile Sources. This is the SCC1 designation. The following 2 digits, “70”, designate Off-highway Vehicle Diesel. 2270 is the SCC3 designation. The last 4 digits designate the more specific category of Lawn and Garden Equipment. 2270004000 is the SCC6 designation. The final “41” designates Rear Engine Riding Mowers (Commercial). This is the most specific designation, SCC8. Some sources are reported as SCC6 but most are reported as SCC8.

Since the inventory is reported as total reactive VOCs, the emissions need to be speciated. This was accomplished using speciation profiles provided by the TCEQ. The profiles list the mass fraction of individual compounds/mixtures for different SCC codes. Many of the speciation profiles are given for SCC6 or SCC8 level source classifications. When SCC8 codes in the inventory did not have matching speciation profiles the codes were converted from SCC8 to SCC6 by ignoring the last 3 digits. This method captured the majority of the unspciated emissions in the inventory. For area and non-road sources, only the top 115 species were considered as SOA precursors. Table 2 shows a summary of the characteristics of the area and nonroad source inventory.

Table 2: Area and non-road source inventory

	Tons/day	% of total
Total area and nonroad emissions in study area	559	100%
Total emissions with speciation profiles*	513	92%
Emissions designated as unidentified after speciation	24	4%
Emissions of top 115 compounds/mixtures	462	83%
Emissions from SOA precursor compounds/mixtures	150	27%
Emissions from SOA precursors with FAC estimates	120	22%
Emissions from SOA precursors without FAC estimates	30	5%

* After all sources with no matching profiles were converted from SCC8 to more general SCC6

Mobile Sources

Mobile source emissions data were taken from a 2000 inventory performed by the TCEQ using the MOBILE model (TCEQ, 2002). Mobile source emissions were assembled by county and were broadly segregated into gasoline emissions and diesel emissions. For gasoline vehicles, the emissions were further segregated into exhaust emissions and running losses (85%), and gasoline vapor emissions largely due to diurnal cycling (15%). Speciation data were collected during the Texas Air Quality Study 2000 (TEXAQS 2000), a major field study performed in southeast Texas. Using measurements taken in a roadway tunnel, mass fractions for individual VOCs emitted during gasoline vehicle operation (exhaust emissions and running losses) were estimated. Diesel contributions to these profiles were minimized because height restrictions in the tunnel limited diesel traffic. In addition, the limited diesel contributions to the speciation profile obtained in the tunnel were subtracted by making measurements at high and low diesel fractions in the fleet passing through the tunnel and extrapolating mass fractions to zero diesel contribution. Details are described by McGaughey, et al. (2002).

Gasoline vapor compositions were determined, in the same study (McGaughey, et al., 2002), by sampling three grades of gasoline from four gasoline marketers (12 samples) and determining whole gasoline composition and gasoline vapor composition. Composite vapor profiles were determined by weighting the data available on each gasoline grade by the fraction of the gasoline market accounted for by that grade. Data from all four gasoline marketers were weighted equally.

For diesel fuel, only exhaust profiles were considered. This approximation should be reasonable since VOC emissions from the diesel fleet are estimated to account for only about 2% of the total on-road mobile source emissions (TCEQ, 2002). The mobile source inventory data are summarized in Table 3.

Table 3: Mobile source emissions analysis.

	Tons/day	% of total
Total mobile source emissions in study area	246	100%
Total emissions with speciation profiles	246	100%
Emissions designated as unidentified after speciation	17	7%
Emissions from SOA precursor compounds/mixtures	73	30%
Emissions from SOA precursors with FAC estimates	63	26%
Emissions from SOA precursors without FAC estimates	10	4%

Estimates of SOA formation

Fractional Aerosol Coefficients Fractional aerosol coefficients were developed by Grosjean and Seinfeld (1989) and are widely used in regional photochemical models (Seigneur, et al, 1997). Grosjean and Seinfeld (1989) and Grosjean (1992) predicted average aerosol composition by using emission inventories and their knowledge of the photochemistry of gas-phase hydrocarbon emissions. The FAC is defined as the fraction of SOA that would result from the emissions of a particular gas phase hydrocarbon (VOC).

$$\text{FAC} = [\text{SOA}] / ([\text{VOC}]_0 * \text{Fraction of VOC reacted}) \quad \text{Equation 1}$$

Where $[\text{VOC}]_0$ is the emission rate of VOC and $[\text{SOA}]$ is the formation rate of SOA.

FACs are generally assumed to be constant, and therefore, the implicit assumption is that the fraction of the emitted VOC that reacts and the yield of SOA from the reactions are constant. While this is clearly an over-simplification, use of FACs provide an order of magnitude estimate of SOA formation rates from individual precursors, and an indication of the relative importance of different precursors in SOA formation.

Estimate of SOA using a gas/particle partitioning model

There are a number of limitations to using FACs to estimate SOA formation. These include assumptions concerning extent of reaction and the extent of partitioning of semi-volatile products into the aerosol phase.

The limitations associated with assuming a fixed partitioning between particle and gas phases can be addressed for some compounds using the modeling framework developed by Odum, et al (1996, 1997). This approach assumes that gas/particle partitioning can be described using an equilibrium partitioning coefficient (Odum et al., 1996, Pankow, 1994). In this analysis, the amount of semi-volatile product that is produced from any single precursor is a function of 4 adjustable parameters (α_1 , α_2 , K_{om1} , and K_{om2}). Two of the 4 parameters (α_1 , α_2) are the yields of two categories of semi-volatile products produced by a selected aerosol precursor gas (VOC). The remaining two parameters, K_{om1} , and K_{om2} , are the equilibrium partitioning coefficients for the two semi-volatile products. Odum et al. (1996) showed that the yield of SOA from a selected VOC

($\Delta\text{SOA}/\Delta\text{VOC}$) was the sum of the yield from each of the semivolatile products (Y_i), and depended on the mass of particulate matter initially present (M_0).

$$\sum_i Y_i = M_0 \sum_i \frac{(\alpha_i K_{om,i})}{1 + K_{om,i} M_0} \quad \text{Equation 2}$$

Odum, et al. (1996) fit data from environmental chamber experiments to determine the 4 adjustable parameters (α_1 , α_2 , K_{om1} , and K_{om2}). In this work, the parameters for pinenes, toluene, trimethylbenzenes, xylenes, and ethylbenzene will be used to estimate SOA yield. These compounds were chosen because they were identified as leading to high rates of SOA formation using the FAC approach and because values for the 4 adjustable parameters (α_1 , α_2 , K_{om1} , and K_{om2}) were available. SOA yields at a variety of total aerosol concentrations (M_0) were estimated and compared to the results obtained using FACs.

Simulation of SOA formation using the modified SOA/SAPRC mechanism

Although the approach devised by Odum et al. (1996, 1997) accounts for variability in gas/particle partitioning based on the amount of aerosol phase available (M_0), it requires an estimate of the extent of reaction (ΔVOC) and does not account for variability in the yield of SOA as a function of the extent of reaction. The latter effect may be particularly important for aromatics where SOA formation results from a series reaction involving dicarbonyl intermediates.

The extent of reaction of the hydrocarbon depends on the rates of reaction of the compound with ozone, hydroxyl radical and other gas phase oxidants. The concentrations of the oxidants and the rates of reaction depend, in turn, on the overall composition and reactivity of the atmosphere in which the SOA precursor is reacting. Therefore, to account for the extent of reaction of aerosol precursors in determining aerosol yields, it is necessary to integrate the SOA formation chemistry into a comprehensive model of gas phase photochemistry. In this work, SOA formation mechanisms were integrated into the model of gas phase chemistry developed by the Statewide Air pollution Research Center (SAPRC) of the University of California. SAPRC has developed software, SAPRC 99, to model the gas phase chemistry of mixtures of more than 350 common air pollutants (Carter, 2000). The atmospheric photoreactions of alkenes, alkanes, aromatics, alcohols, ethers, and other compounds representative of the range of reactive organics emitted into atmosphere are included in SAPRC mechanism. A description of SAPRC 99 is given by Carter (2000).

Chemical mechanisms for SOA formation from lumped aromatic precursors were integrated into the SAPRC mechanism. Aromatics were chosen because previous work and the results of the FAC-based analyses reported here, have suggested that aromatics are significant SOA precursors (Pandis et al., 1992). Furthermore, SOA formation mechanisms from aromatic precursors are primarily due to reactions of aromatics with hydroxyl radicals and other pathways can be assumed to be much less important, simplifying the mechanism development. Chemical mechanisms for SOA formation were developed based on data observed in smog chamber experiments (e.g., Eusebi,

1996; Dekermenjian et al., 1999). Rate parameters were derived from literature values or estimated using group contribution methods (Atkinson, 1985, 1986). The partitioning of semivolatile products from aromatics-OH⁻ reactions was modeled using the partitioning framework developed by Pankow (1994) and Odum (1996). Full details are provided elsewhere (Dechapanya, 2002; Dechapanya, et al., 2002a,b).

With a coupled gas phase and SOA formation mechanism available, it was possible to examine the effect of emission reduction strategies on SOA formation. The first step in this assessment was to develop a base case box model simulation, designed to be representative of the Houston area. Various environmental and chemical measurements made during the Texas Air Quality Study (TexAQS, University of Texas, 2002) were employed in order to develop the initial conditions associated with the basecase box model. Initial concentrations of NO, NO₂, O₃, peroxyacetyl nitrate (PAN), peroxypropyl nitrate (PPN), peroxyethacryloyl nitrate (MPAN) and peroxy-*iso*-butyl nitrate (PiBN) used in the base case were based on measurements made at the LaPorte airport during TexAQS. The LaPorte airport is located just to the south of the heavily industrialized Ship Channel in eastern Houston, a few kilometers northwest of Galveston Bay. The site is strongly influenced by industrial emissions, but air pollutant concentrations are frequently moderated by a strong bay breeze. Concentrations used as initial conditions in the box model were based on data collected between 06:30 and 07:30 of each day between August 25 and September 2, 2002 (Williams, 2002). The 1-second data were averaged over this period, resulting in the concentrations shown in Table 4.

Table 4. Average morning concentrations at LaPorte airport site (August 25-September 2, 2000)

Species	Concentration (ppb)
O ₃	6.3
NO	24
NO ₂	21
PAN	0.065
PPN	0.0073
MPAN	0
PiBN	0

Initial concentrations of PAN related compounds were assumed to be negligible for the base case box model simulations. The consistency of the NO, NO₂ and O₃ concentrations was assessed by calculating O₃ concentration based on measurements of NO and NO₂ concentrations, actinic flux measurements, and an assumption of photochemical steady state. The calculated O₃ concentration was 2.6 ppb, which is in reasonable agreement with measured value, 6.3 ppb. The final choices for initial concentrations of NO, NO₂, O₃ were based on average measured values of NO and NO₂, and ozone concentrations based on a photochemical steady state and the actinic flux calculated internally by the SAPRC model.

Initial concentrations of volatile organic compounds used in the simulations were based on samples collected by an aircraft operated by Baylor University. The samples used in the analysis were collected in canisters near the Laporte airport on six mornings during TexAQS period. All samples were taken at an elevation below 20 m. The air samples in the canisters were subsequently concentrated by cryofocussing and analyzed using gas chromatography (flame ionization and mass spectroscopy detection) (methods described by Lonneman, 1998). These VOC species were then aggregated into the “lumped” hydrocarbon species used in the SAPRC model. Initial concentrations of these lumped species are reported in Table 5.

The simulation also required information on temperature, humidity and mixing heights. Temperature and humidity data were obtained from radiosonde observations collected in downtown Houston and LaMarque (Argonne National Laboratory, 2002). LaMarque is located in Texas City, west of Galveston Bay, and within 10 miles of the Gulf of Mexico. Temperature data from 500 m were used in the simulations; humidity data were averaged over elevations between 200 and 250 m. The mixing heights were estimated using radar wind profiler data collected during TexAQS at five monitoring locations (Argonne National Laboratory, 2002). The mixing heights were estimated using the algorithm described by Grimsdell et al. (1998) and were provided by Wayne Angevine of NOAA/ETL (Angevine, 2002). The data collected between August 25 and September 2, 2000, at two inland sites (Liberty and Wharton), were used to estimate the evolution of mixing heights for the base case simulation.

Table 5. Initial lumped VOC concentrations

Species	Description	ppb	nC*	ppb C
CCHO	Acetaldehyde	2.6	2.00	5.2
ACET	Acetone	5.5	3.00	16.6
MEK	Ketones and other non-aldehyde products $k_{OH} < 5 \cdot 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$	0.7	4.00	2.7
MEOH	Methanol	7.5	1.00	7.5
BALD	Aromatic aldehydes (e.g. benzaldehyde)	0.2	7.00	1.6
ETHENE	Ethene	10.	2.00	20.0
		0		
ISOPRE NE	Isoprene	0.1	5.00	0.7
ALK1	Alkane and other non-aromatic compounds that react only with OH, and have $k_{OH} < 5 \cdot 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$ (Primarily ethane)	16.	1.99	32.8
		5		
ALK2	Alkane and other non-aromatic compounds that react only with OH, and have $5 \cdot 10^2 < k_{OH} < 2.5 \cdot 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$ (Primarily propane and acetylene)	12.	2.71	33.6
		4		
ALK3	Alkane and other non-aromatic compounds that react only with OH, and have $2.5 \cdot 10^3 < k_{OH} < 5 \cdot 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$	10.	4.16	41.7
		0		
ALK4	Alkane and other non-aromatic compounds that react only with OH, and have $5 \cdot 10^3 < k_{OH} < 1 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	11.	5.67	65.1
		5		
ALK5	Alkane and other non-aromatic compounds that react only with OH, and have $k_{OH} > 1 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	6.4	8.17	52.0
ARO1	Aromatics with $k_{OH} < 2 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	5.2	6.82	35.5
ARO2	Aromatics with $k_{OH} > 2 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	4.3	9.00	38.6
OLE1	Alkenes (other than ethane) with $k_{OH} < 7 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	2.9	3.94	11.6
OLE2	Alkenes with $k_{OH} > 7 \cdot 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	2.7	5.03	13.4
TRP1	Terpenes	0.1	10.0	0.9
		0		
ALD1	Aldehydes	1.9	5.68	10.8
KET1	Ketones	0.4	6.73	2.7
INERT	**	n/a	n/a	106.
				1
Sum		101	3.89	499.
				0

* Number of carbons

** INERT species accounts for either species with negligible reactivity and portion of low reactivity species that is treated unreactive for the purpose of lumping (Carter, 1988)

In addition to the ozone precursors associated with the initial conditions, emissions were added continuously in the box model simulation. Emissions were assumed to be constant during the day. The composition of the VOC emissions was assumed to be the same as

the initial conditions. The ratio of NO to NO₂ in the emissions was assumed to be 9:1 on a molar basis. The mass of VOC and NO_x emitted over the course of the day was three times the amount represented by the initial conditions (93.4 kg VOC in initial air, 280 kg per day of VOC emissions, and 18.3 kg NO_x in initial air and 54.9 kg per day of NO_x emissions in the 1 km² area). Photolysis rates are calculated with the simulated actinic flux at 640 meters and deposition was assumed to be negligible. The daily maximum ozone concentration for the base case was predicted to be 95 ppb. Figure 3 shows temporal evolution of ozone, VOC and NO_x mixing ratios for the base case scenario.

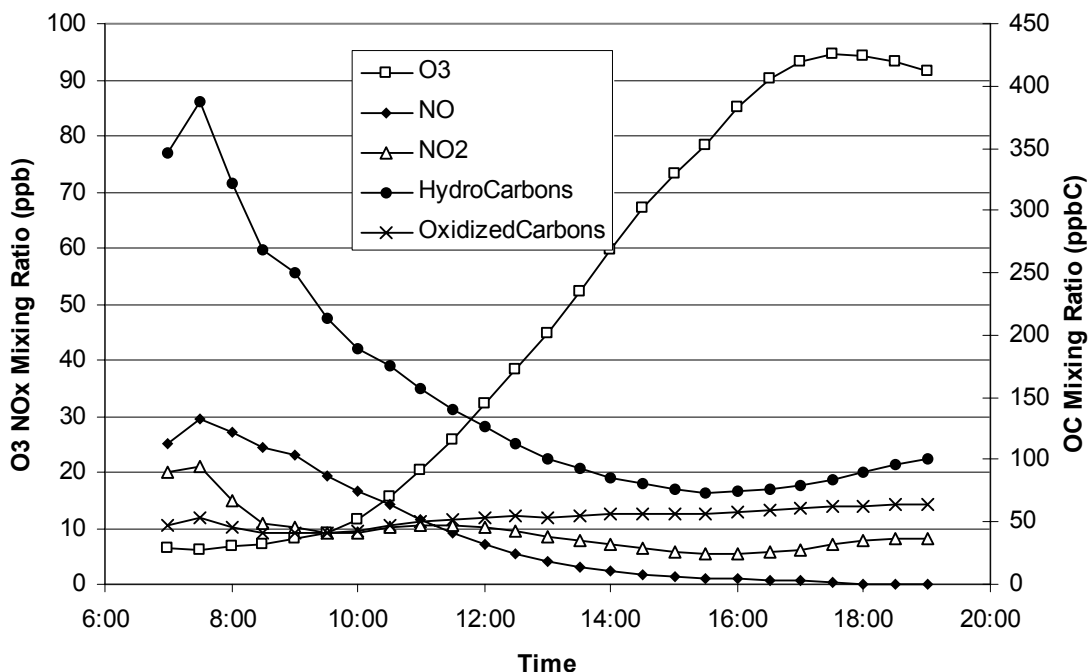


Figure 3. Time series of ozone and ozone precursor concentrations in the basecase simulation

Using this gas phase scenario as the base case for the simulations, the SOA yields for lumped aromatic species (ARO1 and ARO2 in Table 5) were estimated. To examine the sensitivity of the SOA formation to emission reductions, simulations were performed where VOC emissions were reduced, across the board, by 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100%. Similarly, simulations were performed where NO_x emissions were reduced, across the board, by 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100%, and all combinations of these reduction scenarios were considered. This resulted in a total of 121 separate simulations. The results were organized into an isopleth diagram, showing SOA formation levels, as a function of these reduction levels.

In addition to this primary base case and sensitivity studies, additional simulations were performed replacing the VOC mix reported in Table 5 with pure xylene. Total VOC concentration was held constant at 499 ppbC. This case was considered because

observational data in Houston show that, on some occasions, receptor sites are dominated by single industrial sources. This set of simulations with pure xylene was designed to be representative of a reactive plume of aerosol precursors. The same emission reduction scenarios as considered for the primary base case were used for this simulation.

Results and Discussion

Estimates of anthropogenic SOA

The estimates of SOA formation, based on FACs, due to point, area and non-road, and mobile sources for the Houston-Galveston area are reported in Tables 6-10. Table 6 lists emissions and organic aerosol mass (kg/day) for individual compounds for area/non-road and point sources. Table 7 reports emissions and organic aerosol mass (kg/day) for individual compounds for mobile sources. The emissions of SOA precursors for all sources are 200,000 kg/day. Area and non-road mobile sources contribute 56%, mobile sources contribute 27%, and point sources contribute 16%. Estimated secondary organic aerosol mass for all three sources is 3000 kg/day. Though point sources contribute only 16% of the precursor emissions, they produce the highest fraction of SOA mass (53%). SOA mass generated from precursors released by area and non-road and mobile sources contributed 37 and 10%. As shown in Tables 6 and 7, the precursors that contribute most significantly to SOA are aromatics (especially toluene, xylenes and trimethylbenzenes) and anthropogenic terpene emissions from point sources. Table 8 presents the estimates of precursor emissions and SOA formation rates by SCC3 source category from point sources. Pulp and paper and wood product categories are the dominant source of SOA. Table 9 lists SOA formation rates at the SCC6 level for mobile sources. Approximately 50% of the SOA from on-road mobile sources is produced from light duty gasoline vehicles. Table 10 reports SOA formation at the SCC6 level for area and non-road mobile sources, where off-highway vehicle diesel produce most of the aerosol mass, followed closely by the lawn garden equipment and off- highway 2 stroke and 4 stroke gasoline vehicles.

It is difficult to directly compare the SOA formation rates predicted in Tables 6-10 to observed ambient concentrations, however, a semi-quantitative comparison to ambient measurements can be based on elemental carbon concentrations and diesel emissions. To perform the comparison, note that diesel fuel consumption led to emissions of 600 kg of elemental carbon emissions/day in the 8-county Houston non-attainment area (Dennis, et al., 2002). The annual average concentration of elemental carbon is approximately $1.6 \mu\text{g-C}/\text{m}^3$ (Tropp et al., 1998, Dennis et al., 2002). Assuming that all elemental carbon is due to diesel combustion leads to a relationship between emission rate over the core Houston area and observed concentration (600 kg/day yields $1.6 \mu\text{g}/\text{m}^3$). This ratio of carbon emissions to atmospheric concentration can also be assumed to apply to SOA due to precursors released in the core area. If the formation rate of SOA in the core area is approximately two thirds of the 3000 kg/day over the entire domain, then a SOA concentration of less than $5 \mu\text{g}/\text{m}^3$, would be expected. This is likely to be an upper bound since diesel is not the only source of EC in the region. An upper bound concentration of $5 \mu\text{g}/\text{m}^3$ for SOA is reasonably consistent with the OC and EC data presented in Figure 1.

Table 6: Estimates of anthropogenic SOA for individual compounds (all units are kg/day)

Compounds	area (kg/day)		point (kg/day)		Total SOA	Total Emiss
	SOA	Emiss	SOA	Emiss		
Terpenes,Unspec			679.5	6291.7	679.5	6291.7
B-PINENE			369.4	1231.2	369.4	1231.2
A-PINENE			360.2	1200.8	360.2	1200.8
ISOMERS OF XYLENE			45.0	3853.7	45.0	3853.7
TOLUENE	286.2	44168.9	42.5	6566.0	328.8	50734.9
ETHYLBENZENE	15.1	1862.7	12.4	1530.6	27.5	3393.3
PHENOL			11.7	507.1	11.7	507.1
M-XYLENE	12.0	637.6	11.4	606.7	23.4	1244.3
O-XYLENE	82.8	6371.3	9.9	762.3	92.7	7133.6
NAPTHALENE	29.6	2311.9	5.8	455.6	35.4	2767.6
METHYL-T-BUTYL ETHER			4.5	4733.6	4.5	4733.6
CUMENE (ISOPROPYL BENZENE)			4.1	789.1	4.1	789.1
TRIMETHYLBENZENE	11.4	661.4	3.0	177.2	14.4	838.6
N-DODECANE	8.8	1122.9	3.0	381.8	11.7	1504.7
P-XYLENE	14.1	3156.6	2.7	610.9	16.9	3767.5
C8 PHENOLS			2.6	154.1	2.6	154.1
N-TRIDECANE			2.6	261.9	2.6	261.9
CHLOROBENZENE			2.0	314.9	2.0	314.9
N-UNDECANE	6.8	1093.7	2.0	313.8	8.8	1407.5
C10H12			1.8	167.7	1.8	167.7
NONANE	2.0	669.1	1.4	472.5	3.4	1141.6
P-DICHLOROBENZENE			1.0	223.3	1.0	223.3
CYCLOHEXANE	0.7	2762.0	0.7	2841.2	1.3	5603.2
METHYLCYCLOPENTANE	0.3	1493.2	0.1	856.2	0.4	2349.4
HEPTANE	0.7	8675.7	0.1	1664.8	0.9	10340.6
ISOMERS OF DODECANE	0.8	900.3	0.1	161.1	0.9	1061.3
N-DECANE	0.3	688.4	0.1	144.6	0.4	833.0
OCTANE	0.3	2874.8	0.1	601.5	0.4	3476.3
1,2,3-TRIMETHYLBENZENE	14.4	784.5			14.4	784.5
1,2,4-TRIMETHYLBENZENE	34.0	2931.2			34.0	2931.2
1,2-DIETHYLBENZENE	21.1	713.6			21.1	713.6
1,3,5-TRIMETHYLBENZENE	50.3	2343.6			50.3	2343.6
1-METHYL-3-ETHYLBENZENE	23.7	1213.0			23.7	1213.0
2,2,4-TRIMETHYLPENTANE	0.3	2732.6			0.3	2732.6
2,3,3-TRIMETHYLPENTANE	1.5	1293.8			1.5	1293.8
2,3-DIMETHYLPENTANE	0.1	1760.3			0.1	1760.3
2,4-DIMETHYLHEXANE	0.7	7242.9			0.7	7242.9
2,5-DIMETHYLHEPTANE	0.9	838.9			0.9	838.9
2-METHYL-3-HEXANONE	1.1	3366.3			1.1	3366.3
2-METHYLDECANE	8.3	1320.9			8.3	1320.9

3,4-DIMETHYLOCTANE	0.4	826.4		0.4	826.4
3-METHYLHEXANE	0.1	1401.6		0.1	1401.6
C10 AROMATIC	66.8	2255.9		66.8	2255.9
C10 COMPOUNDS (DIESEL EXHAUST)	3.8	852.7		3.8	852.7
C11 COMPOUNDS (DIESEL EXHAUST)	5.4	867.3		5.4	867.3
C13 COMPOUNDS (DIESEL EXHAUST)	3.7	830.9		3.7	830.9
C14 COMPOUNDS (DIESEL EXHAUST)	9.5	1078.0		9.5	1078.0
C15 COMPOUNDS (DIESEL EXHAUST)	10.0	1053.8		10.0	1053.8
C16 COMPOUNDS (DIESEL EXHAUST)	11.0	845.5		11.0	845.5
C17 COMPOUNDS (DIESEL EXHAUST)	207.6	741.3		207.6	741.3
C7 COMPOUNDS (DIESEL EXHAUST)	7.3	700.1		7.3	700.1
C7 CYCLOPARAFFINS	0.2	2342.8		0.2	2342.8
CYCLOPENTANE	28.8	766.7		28.8	766.7
CYCLOPENTENE	34.0	905.4		34.0	905.4
DIMETHYLCYCLOHEXANE	0.4	3961.7		0.4	3961.7
ETHYLCYCLOHEXANE	4.7	1454.5		4.7	1454.5
INDANE	3.0	639.0		3.0	639.0
ISOMERS OF BUTYLBENZENE	4.5	964.7		4.5	964.7
ISOMERS OF NONANE	0.1	2505.3		0.1	2505.3
ISOMERS OF OCTANE	0.2	1889.0		0.2	1889.0
M-DIETHYLBENZENE	20.8	700.8		20.8	700.8
METHYLNAPHTHALENES	5.4	636.4		5.4	636.4
NONENONE	7.5	668.9		7.5	668.9
TRIMETHYLCYCLOHEXANES	5.8	1607.8		5.8	1607.8
xylene(s)	91.5	7835.7		91.5	7835.7

Table 7: Estimates of SOA formation for mobile sources (kg/day)

	diesel exhausted		gasoline exhausted		gasoline vapor		Total emiss	Total SOA
Compound	emiss	SOA	emiss	SOA	emiss	SOA		
1,2,4-Trimethylbenzene	166	1.9	1852	21.5	65	0.8	2084	24.2
1,3,5-Trimethylbenzene	52	1.1			33	0.7	85	1.8
1-Methylcyclopentene					65	3.1	65	3.1
2,2,4-Trimethylhexane					33	0.0	33	0.0
2,2,4-Trimethylpentane	121	0.1	5557	6.5	883	1.0	6561	7.7
2,2-Dimethylpentane					33	0.0	33	0.0
2,3,4-Trimethylpentane	41	0.0	1852	2.2	294	0.3	2187	2.6
2,4,4-Trimethyl-1-pentene					33	1.0	33	1.0
2,5-Dimethylheptane					33	0.0	33	0.0
2-Methylheptane	25	0.0			65	0.0	90	0.0
2-Methyloctane					33	0.1	33	0.1
3-Methylheptane	22	0.0	1852	0.9	98	0.0	1973	1.0
3-Methyloctane					33	0.1	33	0.1
cis-2-Heptene					33	0.3	33	0.3
Cyclohexane					98	0.0	98	0.0
Cyclopentene	10	0.4			98	3.7	109	4.1
ethylbenzene	88	0.7					88	0.7
Ethylbenzene			1852	15.0	65	0.5	1918	15.5
Ethylene					33	0.0	33	0.0
isopropylbenzene	16	0.1					16	0.1
m- & p-Xylene			5557	59.6	229	2.5	5786	62.0
m,p-xylene	330	3.5					330	3.5
Methylcyclohexane			1852	6.0	164	0.5	2016	6.5
Methylcyclopentane	59	0.3	1852	0.3	458	0.1	2370	0.7
m-Ethyltoluene			1852	36.2	33	0.6	1885	36.9
n-Butane			1852	0.0			1852	0.0
n-Heptane			1852	0.2	229	0.0	2081	0.2
n-nonane	3	0.0					3	0.0
n-Octane					65	0.0	65	0.0
Nonane					33	0.1	33	0.1
n-propylbenzene	26	0.1					26	0.1
o-Xylene	126	1.6	1852	24.1	98	1.3	2077	27.0
Toluene	446	2.9	9262	60.1	851	5.5	10558	68.5
trans-3-Heptene					33	0.3	33	0.3

Table 8: Estimates of SOA formation at SCC3 level for point sources

SCC1_DESC	SCC3_DESC	SOA(kg/d)	Emiss(kg/d)
Industrial Processes	Pulp and Paper and Wood Products	1406.2	12259
Industrial Processes	Petroleum Industry	45.2	40856
Petroleum and Solvent Evaporation	Petroleum Product Storage at Refineries	43.5	26626
Industrial Processes	Chemical Manufacturing	38.9	69259
Petroleum and Solvent Evaporation	Surface Coating Operations	23.5	6416
Petroleum and Solvent Evaporation	Organic Chemical Storage	6.6	2582
External Combustion Boilers	Electric Generation	5.9	4519
Waste Disposal	Solid Waste Disposal - Commercial/Institutional	4.1	959
Petroleum and Solvent Evaporation	Transportation and Marketing of Petroleum Products	4.0	2525
Industrial Processes	Oil and Gas Production	3.9	5638
Petroleum and Solvent Evaporation	Petroleum Liquids Storage (non-Refinery)	3.2	5337
Waste Disposal	Solid Waste Disposal - Government	2.3	715
Petroleum and Solvent Evaporation	Organic Chemical Transportation	2.0	1629
Industrial Processes	Fabricated Metal Products	1.1	459
Industrial Processes	Cooling Tower	1.1	1157
Industrial Processes	Mineral Products	1.0	834
Internal Combustion Engines	Industrial	1.0	5375
External Combustion Boilers	Industrial	0.6	3153
Industrial Processes	Miscellaneous Manufacturing Industries	0.6	453
Internal Combustion Engines	Electric Generation	0.6	839
Industrial Processes	Secondary Metal Production	0.4	667
Industrial Processes	Rubber and Miscellaneous Plastics Products	0.2	787
Petroleum and Solvent Evaporation	Organic Solvent Evaporation	0.2	636
Industrial Processes	Printing and Publishing	0.2	40
Industrial Processes	Building Construction	0.2	32
Industrial Processes	Primary Metal Production	0.1	1058
External Combustion Boilers	Commercial/Institutional	0.1	224
Waste Disposal	Solid Waste Disposal - Industrial	0.1	277
Industrial Processes	In-process Fuel Use	0.1	59

Table 9: Estimates of SOA formation at SCC6 level for mobile sources

SCC3_DESC	SCC6_DESC	SOA (kg/d)	Emiss (kg/d)
Highway Vehicles - Gasoline	Light Duty Gasoline Vehicles (LDGV)	142	106981
Highway Vehicles - Gasoline	Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)	61	46157
Highway Vehicles - Gasoline	Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)	25	18983
Highway Vehicles - Gasoline	Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)	17	13039
Highway Vehicles - Diesel	All HDDV including Buses (use subdivisions -071 thru -075 if possible)	17	12925
Highway Vehicles - Gasoline	Motorcycles (MC)	4	2894
Highway Vehicles - Diesel	Light Duty Diesel Vehicles (LDDV)	0	90
Highway Vehicles - Diesel	Light Duty Diesel Trucks 1 thru 4 (M6) (LDDT)	0	74

Table 10: Estimates of SOA formation at SCC6 level for area and non-road mobile sources

SCC3_DESC	SCC6_DESC	SOA	Emis
Off-highway Vehicle Diesel	Construction and Mining Equipment	130	9903
Off-highway Vehicle Gasoline, 2-Stroke	Lawn and Garden Equipment	113	34339
Surface Coating	Architectural Coatings	109	25927
Off-highway Vehicle Gasoline, 4-Stroke	Lawn and Garden Equipment	104	31639
Pleasure Craft	Gasoline 2-Stroke	83	25203
Off-highway Vehicle Diesel	Industrial Equipment	46	3547
Surface Coating	Auto Refinishing: SIC 7532	44	8266
Surface Coating	Metal Cans: SIC 341	41	9740
Surface Coating	Other Special Purpose Coatings	32	7678
Surface Coating	Electronic and Other Electrical: SIC 36 - 363	29	6909
Residential	Wood	29	3598
Off-highway Vehicle Diesel	Agricultural Equipment	27	2091
Miscellaneous Non-industrial: Commercial	Pesticide Application: All Processes	27	12803
Miscellaneous Non-industrial: Commercial	Cutback Asphalt	27	4441
Off-highway Vehicle Gasoline, 4-Stroke	Commercial Equipment	26	7944
TSDFs	All TSDF Types	25	12696
Surface Coating	Industrial Maintenance Coatings	23	5474
Off-highway Vehicle Diesel	Lawn and Garden Equipment	21	1626
Surface Coating	Miscellaneous Manufacturing	20	4682
Surface Coating	Wood Furniture: SIC 25	19	4549
Off-highway Vehicle Gasoline, 2-Stroke	Logging Equipment	18	9444
Surface Coating	Metal Coils: SIC 3498	18	4204
Railroad Equipment	Diesel	17	1271
Petroleum and Petroleum Product Storage	Gasoline Service Stations	15	19735
Surface Coating	Traffic Markings	13	3059
Degreasing	All Industries: Cold Cleaning	13	10384
Off-highway Vehicle Diesel	Commercial Equipment	11	850
Pleasure Craft	Gasoline 4-Stroke	11	3239
Off-highway Vehicle Gasoline, 4-Stroke	Industrial Equipment	8	4097
Petroleum and Petroleum Product Storage	All Storage Types: Breathing Loss	7	9530
Surface Coating	Factory Finished Wood: SIC 2426 thru 242	7	1725
Surface Coating	Machinery and Equipment: SIC 35	7	1584
Off-highway Vehicle Gasoline, 2-Stroke	Commercial Equipment	5	1474
Surface Coating	Marine: SIC 373	4	1027
Off-highway Vehicle Gasoline, 2-Stroke	Construction and Mining Equipment	4	2139
Off-highway Vehicle Gasoline, 2-Stroke	Recreational Equipment	3	986
Leaking Underground Storage Tanks	Leaking Underground Storage Tanks	3	4063
Miscellaneous Non-industrial: Commercial	Emulsified Asphalt	3	432
Aircraft	Commercial Aircraft	2	4805
Off-highway Vehicle Diesel	Logging Equipment	2	170
Miscellaneous Industrial	Adhesive (Industrial) Application	2	734
Off-highway Vehicle Gasoline, 4-Stroke	Recreational Equipment	2	574
Off-highway Vehicle Diesel	Airport Ground Support Equipment	2	126
Surface Coating	Motor Vehicles: SIC 371	2	384
Pleasure Craft	Diesel	1	96
Off-highway Vehicle Gasoline, 4-Stroke	Construction and Mining Equipment	1	650
Degreasing	Automotive Dealers (SIC 55): Cold Cleaning	1	1020
Surface Coating	Metal Furniture: SIC 25	1	282
Rubber/Plastics	All Processes	1	212
Degreasing	Fabricated Metal Products (SIC 34): Open Top Degreasing	1	649
Dry Cleaning	All Processes	1	4085

Estimates of SOA using gas/particle partitioning model

The estimates of SOA formation reported in Tables 6-10 are based on FACs, which are based on constant aerosol yields. To examine the potential impact of variability in gas/particle partitioning, the model developed by Odum, et al. (1996,1997) was used to estimate SOA yields at aerosol concentrations ranging from 10 to 30 $\mu\text{g}/\text{m}^3$. SOA yields for selected aromatic and terpene precursors were estimated, using an assumed fraction of precursor reacted consistent with the FAC calculations (Grosjean, 1992). The results are shown in Table 11. SOA yields increase as total aerosol mass (M_0) increases from 10 to 30 $\mu\text{g}/\text{m}^3$, but are consistently lower than the yields based on the FACs (except for 1,2,4 trimethylbenzene).

Table 11: Estimates of SOA for selected compounds

		Using gas/particle partitioning model						Using FACs
		SOA Yields			SOA (kg/day)			
Compounds	Δ VOC	Mo =10	Mo =20	Mo =30	Mo =10	Mo =20	Mo =30	SOA (kg/day)
α -and β -pinene	3999	0.095	0.151	0.193	184	289	369	446
Toluene	7450	0.027	0.042	0.051	202	310	380	402
124-tmb	4302	0.014	0.022	0.028	58	94	120	67
135-tmb	2544	0.014	0.022	0.028	34	56	71	74
o-xylene	2449	0.014	0.022	0.028	33	54	68	122
m-xylene	1206	0.010	0.018	0.024	13	21	29	52
p-xylene	845	0.014	0.022	0.028	11	18	24	52
Ethylbenzene	808	0.027	0.042	0.051	22	34	41	44

Sensitivity of SOA yields to emission reductions

Results of the box model simulations of SOA formation are shown, in the form of isopleth diagrams, in Figures 4 to 6. The x-axis in the Figures shows the level of VOC reductions from the base case emissions, ranging from 0 to 100%. The level of NO_x reductions from the base case is given on the y-axis. Thus, the upper-right hand corner of each diagram represents the base case. Shown in the Figures are lines of constant ozone and SOA concentrations (ozone and SOA isopleths). The daily maximum ozone concentration for the base case is about 95 ppb, and there is a slight NO_x disbenefit, where ozone concentration increases when NO_x emissions are reduced. The maximum SOA concentrations shown in Figures 5 and 6 are only a few tenths of a microgram per cubic meter, based on two different levels of M_0 . These concentrations are lower than those suggested by Figure 1, where OC concentrations of a few micrograms per cubic meter are typical and OC/EC ratios suggest significant contribution of SOA.

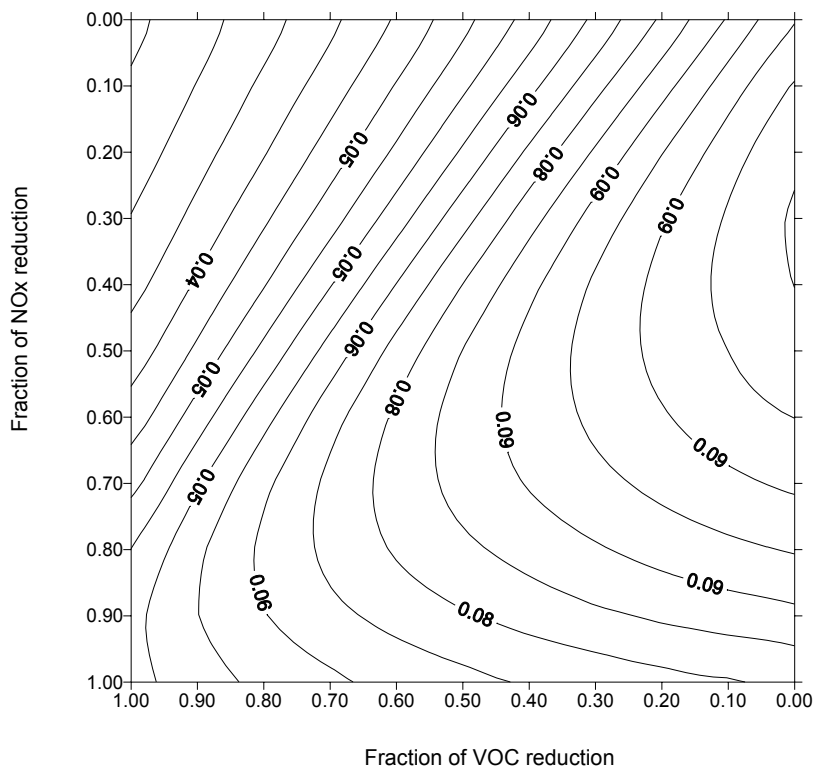


Figure 4: Sensitivity of ozone concentrations to emission reductions for the base case conditions

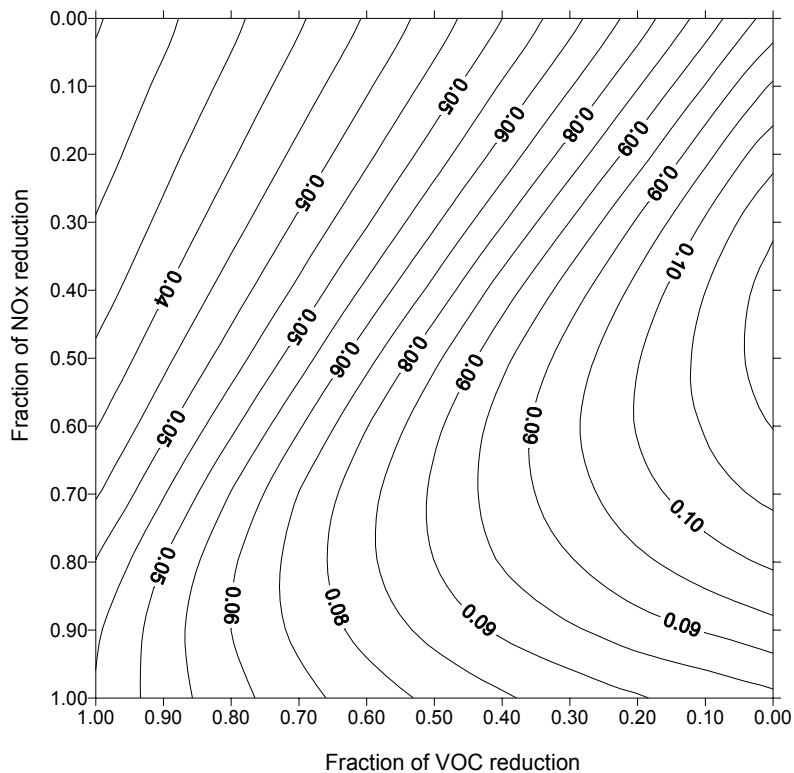


Figure 5: Sensitivity of SOA ($M_{\text{initial}} = 5 \mu\text{g}/\text{m}^3$) to emission reductions for the base case

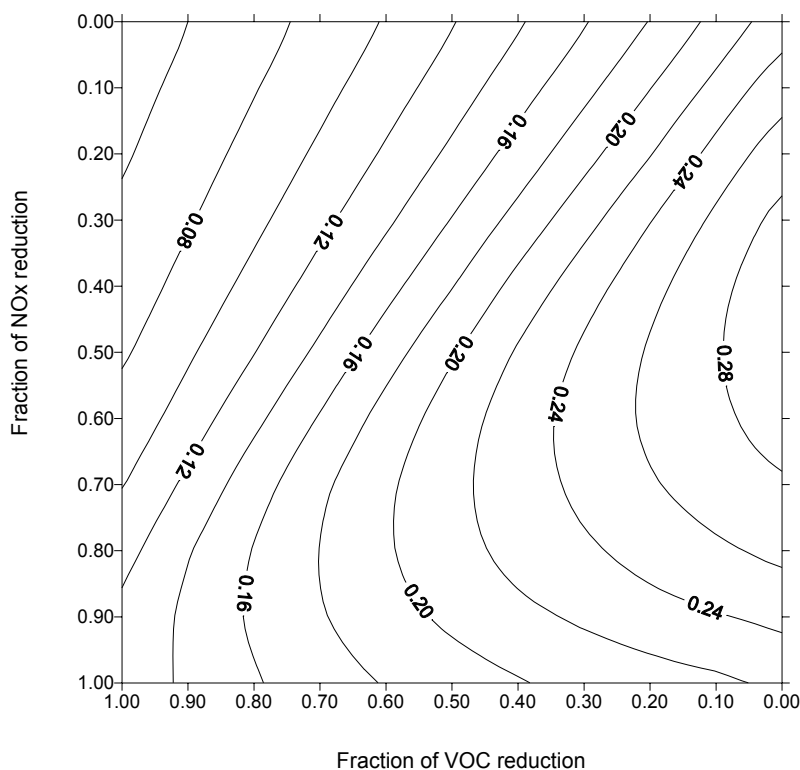


Figure 6: Sensitivity of SOA ($M_{\text{initial}} = 15 \mu\text{g}/\text{m}^3$) to emission reductions for the base case

Figures 7 and 8 show the results of simulations where all of the VOCs were assumed to be xylene. This case was considered because observational data in Houston show that, on some occasions, receptor sites are dominated by single industrial sources. This set of simulations with pure xylene was designed to be representative of a reactive plume of aerosol precursors. The ozone and SOA concentrations reported in Figures 7 and 8 are significantly higher than in Figures 4-6, and the SOA yields in Figure 8 are more consistent with the OC and EC data reported in Figure 1. The SOA yields, coupled with the FAC analyses, suggest that the majority of SOA formation in the Houston-Galveston area is not due to the type of average hydrocarbon concentrations represented in the base case, but are the result of specific emissions of aromatic and terpene SOA precursors.

Another feature to note in Figures 4-8 is the shape of the isopleths. Comparison of the shapes of the ozone and SOA isopleths suggests that the responses of SOA and ozone concentrations to VOC and NO_x emission reductions will be similar and that emission reduction strategies designed to reduce ozone will likely reduce SOA.

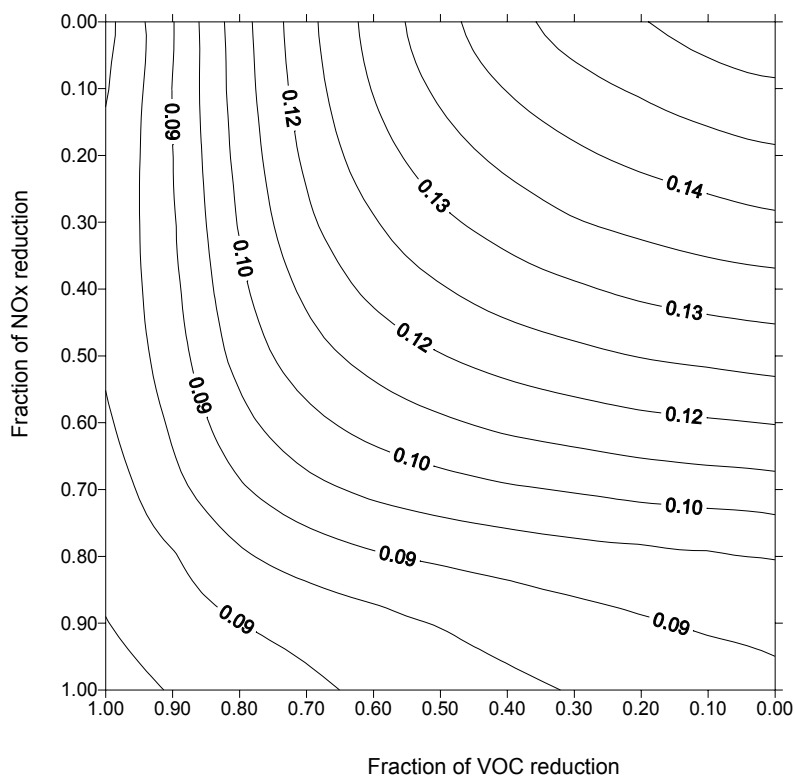


Figure 7: Sensitivity of ozone concentrations to emission reductions for the xylene-rich case

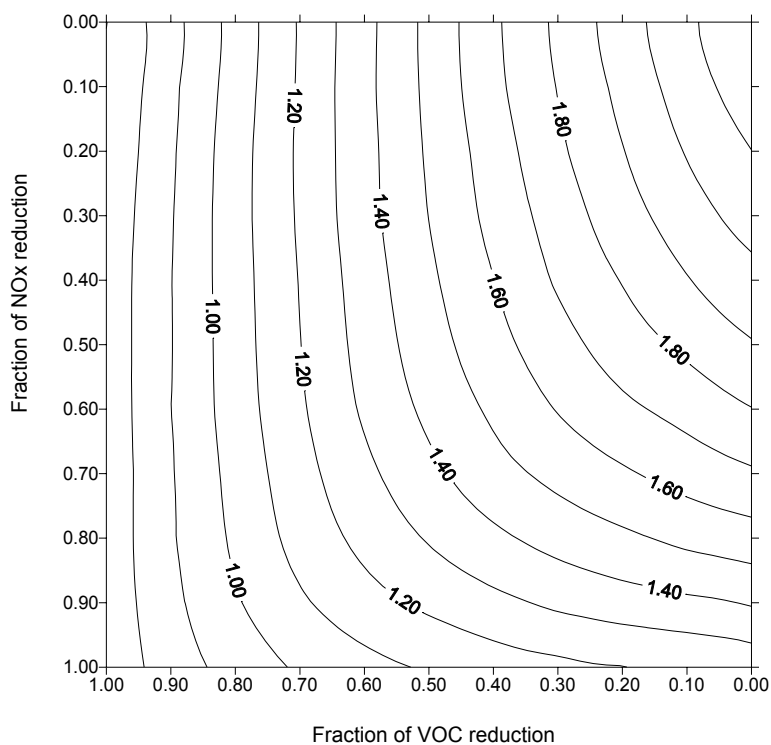


Figure 8: Sensitivity of SOA ($M_{\text{initial}} = 15 \mu\text{g}/\text{m}^3$) to emission reductions for the xylene-rich case

Conclusion

Estimates of SOA formation using a variety of approaches suggest that the main sources of anthropogenic SOA precursor emissions in the Houston area will be point sources, particularly those that emit aromatics and terpenes. Mobile (on- and non-road) and area sources are also expected to be significant sources of SOA. Results of box model simulations, including SOA formation mechanisms and gas/particle partitioning, suggest that SOA formation is sensitive to both aromatic precursor emissions and NO_x emissions, and the pattern of the sensitivity is similar to the pattern of ozone sensitivity to hydrocarbon and NO_x emissions for the Houston area.

References

- Angevine, W. Personal communication, NOAA Aeronomy Laboratory, 2002
- Argonne National Laboratory "Texas AQS Boundary Layer Winds Data Hub", available at: <http://www.atmos.anl.gov/TEXAQS/>, accessed on January 25, 2002
- Atkinson, R. (1985). Kinetics and mechanisms of the gas phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.*, 85: 69-201.
- Atkinson, R. (1986). Estimations of OH radical rate constants from H-atom abstraction from C-H and O-H bonds over the temperature range 250-1000 K, *Int. J. Chem. Kinet.*, 18: 555-568.
- Carter, W. P. L. (2000). Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment: Report to California Air Resources Board Contract 92-329, 95-308,
- Dechapanya, W.; Eusebi, A.; Kimura, Y.; Allen, D.T. (2002a). Secondary Organic Aerosol Formation from Aromatic Precursors: Part I – Mechanisms for Individual Hydrocarbons, *Environ. Sci. & Tech.* Submitted
- Dechapanya, W.; Eusebi, A.; Kimura, Y.; Allen, D.T. (2002b). Secondary Organic Aerosol Formation from Aromatic Precursors: Part II – Mechanisms for Lumped Species, *Environ. Sci. & Tech.* Submitted
- Dechapanya, W. Kinetic and Physical Models of Secondary Organic Aerosol Formation and Their Application to Houston Conditions, PhD Dissertation, The University of Texas at Austin (2002)
- Dekermenjian, M.; Allen, D. T.; Atkinson R.; Arey, J. (1997). FTIR Analysis of Aerosol Formed in the Photooxidation of Naphthalene, *Aerosol. Sci. and Tech.*, 30: 349-363
- Environ Corporation (2001), Final report: Development of source speciation profiles from the TNRCC point source database.

- Eusebi, A. (1996). Composition of Aerosol Formed by the Reactions of Hydrocarbons in Urban Atmospheres: Smog Chamber and Field Measurements, Ph.D. Dissertation, University of California
- Grimsdell, A.W., and W.M. Angevine "Convective boundary layer height measured with wind profilers and compared to cloud base". J. Atmos. Oceanic Technol., 15, 1332-1339 1998
- Grosjean, D. (1992). In Situ Organic Aerosol Formation During a Smog Episode Estimated Production and Chemical Functionality", Atmos. Environ., 26A. 953-963
- Grosjean D.; Seinfeld, J. H. (1989). Parameterization of the Formation Potential of Secondary Organic Aerosols, Atmos. Environ., 23: 1733-1747
- Jimenez, M.; Wilson, G.; Ganesh, Usha.; Coulter-Burke, S. (2002). Final Report: Emissions Processing for the Joint CAXx Photochemical Modeling of Four Southern Texas Near Non-Attainment Areas, Environ International Corporation
- Lonneman, W.A. Comparison of hydrocarbon composition in Los Angeles for the years 1968 and 1997, Conference on Measurement of Toxic and Related Pollutants, Air and Waste Management Association, Cary, N.C., Sept 1-3, 1998.
- McGaughey, G. R.; Desai, N. R.; Allen, D. T. (2002). Analysis of Motor Vehicle Emissions in a Houston Tunnel during the Texas Air Quality Study 2000, Submitted to Atmospheric Environment.
- Neece, J. D. (2001). VOC Speciation Contract, September 19, 2001 H/G B/PA Photochemical Modeling Technical Committee.
- Odum, J. R.; Jungkamp, T. P. W.; Griffin, R.J.; Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. (1997). Aromatic, Reformulated Gasoline, and Atmospheric Organic Aerosol Formation, Environ. Sci. Technol., 31,7: 1890-1897
- Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R.C.; Seinfeld, J.H. (1996). Gas/Particle Partitioning and Secondary Organic Aerosol Yields, Environ. Sci. Technol., 30, 2: 580-585
- Pandis, S. N.; Harley, R. A.; Cass, G.R.; Seinfeld, J. H. (1992). Atmospheric Photochemical Oxidation of 1-Octene: OH, O₃, and O(³P) Reactions, Atmos. Environ., 26A: 2269-2282
- Pankow, J. F. (1994). An Absorption Model of Gas/Particle Partitioning of Organic Compounds in the Atmosphere, Atmos. Environ., 28: 185-188

- Russell, M.M.; Allen, D.T.; Collins, D.R.; Fraser, M.P. (2002). Daily, seasonal and spatial trends in fine particulate matter mass and composition in southeast Texas, Aerosol Sci. and Tech., submitted.
- Seigneur, C.; Pai, P.; Louis, J.F.; Hopke, P.; Grosjean, D. (1997). Review of Air Quality Models for Particulate Matter, American Petroleum Institute Document CP015-97-1b, Washington D.C.
- TexAQS (2002). Website for Texas Air Quality Study, site description available at <http://www.utexas.edu/research/ceer/texaqs/>
- Texas Commission on Environmental Quality (2002). Emission inventories of speciated VOCs point sources in Texas are available at www.tnrcc.state.tx.us/air/aqp/airquality_photomod.html
- Tropp, R. J.; Kohl, S. D.; Chow, J. C.; Frazier, C. A. (1998). Final Report for the Texas PM_{2.5} Sampling and Analysis Study, prepared for Bureau of Air Quality Control, City of Houston, TX,
- Williams, E. personal communication, NOAA Aeronomy Laboratory, 2002